Analyte:	Diisopropylamine	Method No.:	S141
Matrix:	Air	Range:	8.5-37.4 mg/cu m
OSHA Standard:	5 ppm (20 mg/cu m)	Precision ($\overline{CV}_T$):	0.075
Procedure:	Collection in 0.1N sulfuric acid impingers, GC/FID	Validation Date:	10/28/77

1. Principle of the Method

1.1 A known volume of air is drawn through impingers containing 0.1N sulfuric acid to trap the amine vapors present.

An aliquot of the sample solution is neutralized with 0.3N potassium hydroxide and injected into a gas chromatograph equipped with a flame ionization detector.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

This method was validated over the range of 8.5-37.4 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 766 mm Hg using a 120-liter sample volume.

The upper limit of the range of the method is dependent on the collection efficiency. The method is capable of measuring concentrations higher than that noted in Section 2.1 provided the collection efficiency is adequate. Theoretically, if the efficiency of the impinger remains adequate until 90% of the acid is neutralized, 270 mg of diisopropylamine may be collected. This means that an atmosphere containing as much as 2000 mg/cu m can be reliably measured by this method.

3. Interferences

When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time

data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8-37.4 mg/cu was 0.075. This value corresponds to a 1.5 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

A collection efficiency of at least 98% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the impingers was 100.4%. In addition, the samples were found to be stable when stored in the dilute sulfuric acid solution for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the awkwardness in using midget impingers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

The impingers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the impingers during shipping.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

6.1.1 A glass standard midget impinger.

6.1.2 A calibrated personal sampling pump suitable for sampling at 1 liter per minute for 120 minutes. The pump must be accurate to within ±5% at the recommended flow rate. The sampling pump is

protected from splashover or water condensation by a second impinger or bubbler positioned between the exit arm of the impinger and the pump.

6.1.3 Sulfuric acid, 0.1N. Prepare a sufficient amount for collection and transfer of samples.

6.1.4 Pipet, 15-ml or other suitable device for adding 0.1N sulfuric acid to the impingers.

6.1.5 Thermometer.

6.1.6 Barometer.

6.1.7 Stopwatch.

6.2 Gas chromatograph with a flame ionization detector.

Column, (6-ft x 1/4-in O.D. x 2-mm I.D. glass) packed with 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B.

An electronic integrator or some other suitable method for measuring peak areas.

Sample containers with Teflon-lined caps, 2-ml.

Microliter syringes, 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots for dilution.

Volumetric flasks, 25-ml or other convenient sizes for making standard solutions and sample dilutions.

7 Reagents

Diisopropylamine, 99%.

Distilled water.

Sulfuric acid, 0.1N in distilled water.

Potassium hydroxide, 0.3N in distilled water

7.5 Isoamyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in 0.3N potassium hydroxide.

Nitrogen, purified.

Hydrogen, prepurified.

Air, filtered compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative impinger in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Pipet 15 ml of 0.1N sulfuric acid into the first midget impinger.

8.3.2 Assemble the sampling train. Put the first impinger in a suitable impinger holder. The outlet of this impinger is connected by tubing to the inlet of the trap. The outlet of the trap is connected by a short piece of tubing to the pump's inlet. The trap is in a suitable impinger holder which is attached to the pump. Liquid collected in the trap must never be returned to the first impinger.

8.3.3 The air being sampled should not pass through any hose or tubing before entering the first impinger.

8.3.4 A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 120 minutes. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 After sampling, remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1-2 ml of 0.1N sulfuric acid into the midget impinger flask. Repeat this process for liquid collected in the trap. However, do not combine the two solutions in one impinger bottom. Be sure each impinger bottom is properly labeled. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.

8.3.6 Attempt to minimize sample spillage. Do not allow the solution level in the first impinger to fall below 10 ml Replace spilled solution with fresh 0.1N sulfuric acid. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation has probably occurred. Use distilled water to bring the solution volume back up to 15 ml.

8.3.7 With each batch of ten samples submit one midget impinger containing 15 ml of 0.1N sulfuric acid prepared from the same stock as that used for sample collection. This impinger must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this impinger as the blank.

8.3.8 The impingers in which the samples are stored should be shipped in a suitable container designed to prevent damage or leakage in transit.

8.4 Analysis of Samples

8.4.1 Transfer of Sample. Transfer the contents of the impinger into a 25-ml volumetric flask, using 2-3 ml of 0.1N sulfuric acid to rinse the impinger bottle. Add rinse to the volumetric flask, then dilute to the mark with 0.1N sulfuric acid.

8.4.2 Neutralization of Sample. Transfer a 500-microliter aliquot of the acidic sample solution to a 2-ml vial. Add 500 microliters 0.3N potassium hydroxide.

Note: If the internal standard method is used, add the internal standard solution made up in 0.3N potassium hydroxide.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (25 psig) hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 200°C injector temperature
5. 240°C manifold temperature (detector)
6. 125°C column temperature

A retention time of approximately nine minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately sixteen minutes.

8.4.4 Injection of Sample. A 2-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative

such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Sample Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to 25 ml of 0.1N sulfuric acid. The solutions are then neutralized and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm$ 5%.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 120-liter sample at the selected level was used to determine the analytical method recovery. Six volumetrics at each of the three levels (0.5, 1, and 2X the OSHA standard) were spiked with diisopropylamine. A parallel blank was also prepared except that no sample was added to it. All solutions were then neutralized and analyzed as described in Section 8.4.

The sample recovery equals the average weight in mg recovered from the volumetric divided by the weight in mg added to the volumetric, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The average recovery values obtained were at least 97% and as such no recovery correction factor has been used in the determination of the "true" values.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 25 ml 0.1N sulfuric acid because the samples are in this amount of sulfuric acid. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards varying in concentration over the range of interest is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample in order to minimize the effect of variations in FID response. A calibration curve is established by plotting concentration in mg per 25 ml versus peak area.

For the internal standard method, use 0.3N potassium hydroxide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in mg/25 ml.

10. Calculations

Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg per 25 ml and the volume of sample injected is identical to the volume of the standards injected.

Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample solution
mg blank = mg found in blank solution

Divide the total weight by the analytical method recovery to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sample flow rate

t = sampling time

pressure during calibration of sampling pump (mm Hg)

pressure of air samples (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Directory, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.2 Backup Data Report for Diisopropylamine, No. S141, prepared under NIOSH Contract No. 210-76-0123.